Analysis of a novel electron beam lithography resist, SML and its comparison to PMMA and ZEP resists

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Abstract

We present a study on a novel, positive-tone electron beam lithography (EBL) resist known as SLM and compare its lithographic performance to well-established positive resists such as 950K polymethyl methacrylate (PMMA) and ZEP 520A. SML has been fabricated to have similar processing parameters to PMMA, but with enhanced performance. SML resists bears processing parameters very similar to that of PMMA such as film deposition, baking temperatures as well as the developers used for PMMA also work well with SML resist.

Contrast curve measurements were generated for different thicknesses of SLM at exposure voltages. Two temperature variants were employed for developing the resist with 7:3 IPA:water, *viz.* room temperature and 0 °C. To verify the resolution of SML resist, dense gratings of single pixel lines were compared to those fabricated using 950K PMMA and ZEP 520A. Fundamental pattern transfer skills of metal lift-off and dry etching were compared with ZEP resist. Metal lift-off was carried out using 5-10 nm thick chromium metal and 1165 resist remover. The resilience of the SML resist to dry etching (ICP etching system with SF_6 and C_4F_8 gas mixture) was compared to ZEP resist and then dense gratings on both the resists were etched into Si.

The data obtained from the contrast curves show high contrast of the new resist. From the grating results, SML demonstrates very high resolution like ZEP and PMMA. The pattern transfer abilities are also similar and some even superior to that of ZEP resist.

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1. Introduction

The trend in reducing the feature size in microelectronic fabrication has been persistent since prefatory stage of semiconductor device fabrication to avail speedy functionality of devices. [1]. To achieve extremely small feature sizes, nanolithography techniques like electron beam lithography (EBL), nanoimprint lithography (NIL) and focused ion beam lithography (FIB) are currently the most common choices in research and development. EBL is undoubtedly the favourite tool for lithography as it is a direct write method, more flexible as compared to NIL and non-destructive technique compared to FIB, and has a very high resolution as the electron beam can stay well focused below 10 nm beam size [2]. Continuous advances are being made to improve resolution of EBL technique and the main inclination is also towards developing ultra-high resolution resists.

Resists are stencils created by irradiating the electron beam on the polymer thin films rendering the irradiated area soluble (*positive*) or insoluble (*negative*) in developer solvents. The features on resist are transferred exactly on the substrate. Their dimensions and quality are governed to a great extent by the resist properties and the interaction of electrons in the beam with resist components. Resist properties such as sensitivity, contrast, resolution, etch resistance and lift-off efficiency must be considered according to application throughout procedure of EBL fabrication. The resist resolution is chiefly hindered by proximity effect occurring due to the scattering of electrons inside the resist and substrate, thereby inducing unwanted exposure. High acceleration voltages and thin resists are employed to minimize the proximity effect in the resist [3]. However, high voltages result in longer exposure times. Most of the sub 10 nm half-pitch structures are comfortably fabricated on resists such as hydrogen silsesquioxane (HSQ) or Calixarene which are *negative* tone resists [3,4]. Despite of having high resolution both the resists suffer a low sensitivity thus requiring long writing times and moreover, the above two resists are formulated with typically high cost and short shell life [3]. Due to the fact that these resists have low sensitivity, their usage is mainly confined to small scale nano-patterning in R&D.

Poly methy methacylate (PMMA) is a simple, *positive* tone and still a dominant EBL resist. However, it is only under special conditions PMMA is able to produce extremely high resolution structures. Sub 10 nm wide lines have been reported using PMMA with EBL voltages of 80-100 keV [5]. Suchlike resolution is however, unobtainable with lower voltages like 10 keV-30 keV. Another positive tone resist that has gain popularity due to its superiority over PMMA in terms of sensitivity is ZEP resist. This resist is structurally similar to PMMA except the side group which is substituted with a chlorine atom and phenyl group [6]. In addition to a superior sensitivity and resolution, ZEP resist has been reported to have higher plasma etch durability for C_2F_6 and SF_6 gases [6]. ZEP lags behind PMMA because it is more expensive than PMMA.

In this work, a new EBL resist presented by EM Resist Ltd. (Macclesfield, UK), named SML, is studied. It is a positive tone organic resist that has been produced to have similar processing parameters to PMMA, but with enhanced performance. Contrast curves were produced for three thicknesses, *i.e.* 50, 100 and 300 nm, developed at room temperature and 0°C. Although it can be developed using all the standard PMMA developers, 7:3 IPA/water has been reported to be a suitable developer for high contrast and high sensitivity for SML [7]. Hence, the developer used in the current study is 7:3 IPA/water. Existing positive resists, ZEP 520A and PMMA, were chosen to compare the sensitivity, contrast, resolution, etch resistance and lift-off proficiency of SML. This works brings to the forefront the analysis of SML resist and compares its quality to that of ZEP and PMMA resists for semiconductor fabrication.

2. Material and methods

The SML resists of three concentrations i.e. SML 50, 100 and 300 used in this study were provided by EM Resist Ltd. The ZEP520A resist was purchased from Nippon ZEON Corp. and 950PMMA A7 from MicroChem Corp. Bulk silicon substrates of <100> orientation and sized 10 mm×10 mm were used throughout the experiment.

SML resists was spun on the substrates with 4000 rpm for 60 s. The substrates were then soft-baked on a hot plate at 180 °C for 180 s prior to the exposure. PMMA substrates were processed in the same fashion. ZEP resist was also spun at 4000 rpm, but soft-baked at 120 °C. All the exposures within 10-30 kV voltage range were performed on Raith e-LiNE Plus and the 50 kV on JOEL JBX 6000FS. PMMA and SML substrates were developed in a 7:3 IPA:water developer. ZEP was, however, intentionally developed with its recommended ZED-N50 developer since attempts with 7:3 IPA:water lowered its sensitivity up to 12 times. All developments were 15 s long, followed by a 15 s IPA rinse.

For generating the contrast curves, an array of 50 µm × 100 µm rectangles were exposed on the substrates with increments in dose by a factor of 0.07. Post exposure, the substrates were developed using their appropriate developers. For cold temperature developments, all the solvents were cooled in a freezer submerged in an ice-bath until the temperature obtained was 0 °C. The step height in the resist was measured using a DEKTAK Profilometer.

Gratings of single pixel lines spaced with pitch sizes of 30, 40, 60, 80, 100 and 200 nm were exposed on SML, ZEP and PMMA having a thickness of about 50 nm. The exposures were carried out at a 30 kV voltage, the current was 34 to 37 pA with a step size of 2 nm and a 10 µm aperture size. The substrates were imaged on Raith e-line Plus and FEI Helios NanoLab 600 at 10 keV and 5 keV, respectively. Prior to imaging all the substrates were coated with Au/Pd for suave imaging.

For the metal lift-off, 5 and 10 nm thick chromium metal was deposited on SML and ZEP resists having high resolution gratings as described above using electron beam evaporation in a Temescal FC-2000 machine. The lift-off was performed by immersing the substrates in a Microposit remover 1165 (Shipley) for 5 to 10 minutes at 60 °C. The substrates were then washed under flowing deionised (DI) water and nitrogen dried prior to SEM imaging the substrates.

The etching tests were carried out using Plasmalab 100 ICP etching system (Oxford Instruments) with SF_6 and C_4F_8 gas mixture. In order to determine the etch rates of SML and ZEP, ~300 nm thick resists were spun on Si and etched for time intervals of 1, 3, 5 and 7 minutes and the film thicknesses were measured by ellipsometer (M2000-Wollam). Identical aforementioned high resolution gratings were etched using the same recipe for 1 min, since the gratings were written on 50 nm thick resists.

3. Results and Discussion

Table 1 illustrates the sensitivity and contrast values of the SML resist of three different thicknesses, 50, 100 and 300 nm exposed with 10, 15, 25, 30 and 50 kV voltages at room and low temperature. The contrast (γ) values are calculated from the dose values by using the equation $\gamma = [\log_{10}(D_1/D_0)]^{-1}$, where D_0 and D_1 represent the dose values at which the resist thickness is full and zero, respectively [8]. The dose values expressed in table 1 equal to the dose at which the irradiated resist completely developed (D_1). From the sensitivity-contrast values in table 1 in ambient development, it can be interpreted that the contrast values of all the thicknesses appear in the range of 9-10, regardless of increase in voltage or thickness. Nevertheless, it is a common establishment that rise in voltage results in the reduction of sensitivity, a trend that can be seen in table 1 as well. Unexpectedly, the contrast values observed at 50 kV are lower than those at the lower voltages which could be due to the fact that these exposures were carried out on a different EBL system (JOEL).

Cold development has previously shown resolution enhancement in other positive resists like PMMA and ZEP [8, 9]. In order to better understand the influence of cold temperature on the development of SML resist, contrast curves were generated at voltages of 10, 15, 20 and 25 kV using the SML 50 resist that was developed at 0 °C with the 7:3 IPA:water developer (see table 1). These values suggest a decrease in the sensitivity by 4 times at room temperature and a moderate increase in the contrast due to the use of low temperature developers. Thus, low temperature development seems to improve the contrast by approximately 1.6 times.

Next, the contrast curves of SML 300 were compared with those of the standard positive resists ZEP and PMMA having a similar thickness and exposed at the same voltage of 10 kV. It was observed from the contrast curves that ZEP resist showed the highest sensitivity (~22 µC/cm^2) amongst all the resists. The sensitivity of PMMA (~78 µC/cm^2), as expected, lags behind ZEP resist by a factor of ~2.2 while the sensitivity of SML (~ 107 µC/cm2) resist developed in 7:3 IPA:water is almost 5 times lower than that of ZEP resist. The contrast values, on the other hand, show that the SML contrast equals to that of PMMA, *i.e.* ~ 12 and is higher than that of ZEP resist. From this data it can be concluded that SML resist shows poorer sensitivity than the standard PMMA and ZEP resists. The contrast is, however, appreciably high.

In order to investigate the quality of the new resist, high resolution gratings were written on SML and ZEP resists of 50 nm film thickness. The patterned substrates were developed in their respective cold developers as low temperature development improves the resolution.

Since the contrast curves values in table 1 suggest greater contrast with high voltages and cold development, 30 kV voltage (the maximum voltage offered by the Raith e-Line Plus system) was preferred to write the high resolution gratings and together with development in cold developers.

Figure 1 demonstrates scanning electron microscopy (SEM) images of gratings written as single pixel lines with 30 nm pitch size in SML (1a), ZEP (1b) and PMMA (1c) resists. Figures 1d and 1e illustrate the micrographs of the extremely high resolution structures created in the SML and ZEP resists. As observed in figure 1a, 12-16 nm wide lines were deftly written with a space of ~15 nm. The arrays of lines were continuous, straight and neat throughout with very few dwellings where micro-bridging was observed. However, resist clearance from the bottom of the trenches is visibly observed in figure 1a. Trivial widening of linewidths from 18 to 20 nm is observed in pitches greater than 30 nm. However, there was no micro-bridging noticed in greater pitches and the gratings appeared more uniform, sharp, with clean trenches and unceasing lengths than that observed in 30 nm pitch gratings. Furthermore, it was observed that below the optimum dose the linewidth did not reduce but the resist residue remained in the trenches. Identical high resolution gratings exposed on ZEP resist of similar thickness are presented in figure 1b. The linewidth observed throughout the gratings and in all the pitches is 15 nm on an average, without any widening or evident micro-bridging observed. Based on the figures 1a and 1b can be estimated that the quality of gratings in the two resists is comparable. The line edge roughness, however, seems faintly higher in the ZEP resist. From figures 1a and 1b it can be established that resolution as high as 15 nm half pitch is readily achievable in SML resist with a voltage of 30 kV and by engaging the mild 7:3 IPA:water developer. Additionally, the line edge roughness is appreciably lower than in the standard ZEP resist. The next SEM image in figure 1c shows the same gratings exposed on PMMA with identical working conditions. Meagre quality of gratings is observed in this image with evidently high line edge roughness, poor resist clearance from the trenches and larger linewidths from 22 nm up to 30 nm at higher pitches (not shown here). SML resist thus exhibits unrivalled gratings in comparison to PMMA.

Figure 1d shows that 5 nm wide lines were obtained in SML and are the smallest lines reported to date with this resist. Sub 10 nm lines were also achieved in ZEP resist as seen in figure 1e. These results demonstrate that both resists are capable of very high resolution patterning.

In order to inspect the pattern transfer capabilities of the new resist, high resolution gratings on 50 nm thick SML and ZEP resists were subjected to basic etching and metal lift-off techniques. During the metal lift-off it was observed that from pitch size 80 nm and higher the metal was lifted off easily within 60 s in the 1165 remover. However, to completely clear off the resist from smaller pitches, the substrates were immersed in 1165 overnight. Figures 2a and 2b show the metal lines resolved from 5 nm thick chromium metal deposited on SML and ZEP resists, respectively. Dense lines (40 nm pitch) of ~15 nm linewidths were achieved in SML. Metal lines as small as 10 nm were obtained in ZEP resist, which is a very good achievement. The line quality improves slightly with increase in the pitch size in the case of both resists.

In the case of etching, the etch rates of both the resists were compared with 300 nm thickness and subsequently high resolution gratings were etched into silicon substrates. The etch rates of the two resists at various time intervals are demonstrated in Fig. 3. As seen from this figure, the amount of SML consumed initially is lower than that of ZEP resist. However, as time progresses the SML consumption becomes higher than that of ZEP resist. It can also be observed that although ZEP resist has higher etch resistance than SML after 3 minutes, the difference between etch rates in not large. In contrast, the difference in the etch rates at 1 minute is quite notable, also suggesting that SML is a more suitable candidate for shallow etching.

The high resolution gratings were etched for 1 minute using the same recipe. Figures 2c and 2d illustrate the gratings having 60 nm pitch etched into silicon using SML and ZEP, respectively. The results with SML were marginally better than with ZEP resist, which is usually acknowledged for its superior etch resistance than most of the positive tone resists [6]. It can be seen from figures 2c and 2d that etching of dense gratings in Si was easily possible with both the resists. It is to be noted that in the case of ZEP eminent bridging between the trenches was observed throughout the grating with 40 and larger pitches (not shown). This bridging effect was not evident in the case of SML. As the pitch size is increased, the quality of the etched lines recuperates with both resists. However, widening of the Si trenches up to 20 nm occurred with ZEP when compared to the ~15 nm grating linewidth achieved in the resist. Moreover, bridging at few dwellings was also present. These two effects were not observed in the case of SML. Therefore it can be concluded that pattern transfer via etching delivered better results with the SML resist than with ZEP.

4. Conclusions

A detailed characterisation of SML resists has been expressed in this work focusing on its sensitivity and contrast, resolution and pattern transfer abilities. It was established from the contrast studies that this resist bears a high contrast of about 11 with 7:3 IPA:water developer. Additionally, comparison to ZEP and PMMA resists showed that SML's contrast equals to that of the other two but with the lowest sensitivity amongst three.

Single pixel gratings of pitches down to 30 nm exposed on SML showed outstanding quality lines with width of ~15 nm, suggesting its resolution equalling to that of the high resolution ZEP resist. Assessment of SML's etching and metal lift-off ability showed that SML is a good candidate for both the processes. Etch results showed that etching is more uniform with this resist since no line widening and bridging was observed in contrast to ZEP. Using SML, dense metal lines of ~15 nm linewidth are readily achievable with a basic lift-off technique.

This preliminary study on SML can conclude that SML is a proficient EBL resist. The resist properties are similar to the well-established EBL resists, ZEP and PMMA which accounts for its superior quality as an EBL resist.

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Highlights

- Study of a new electron beam resist, SML.
- Contrast is as high as PMMA
- Dense grating with linewidth from ~5-8 nm demonstrated in SML and ZEP
- Etch resistance equivalent to ZEP resist

Figure and Tables Captions

Table 1: Values of clearance dose (D_1) and their corresponding contrasts values (γ) of SML resist with 50, 100 and 300 nm thickness and SML 50 developed at 0°C

Figure 1: High resolution gratings with 30 nm pitch size on (a) SML 50, (b) ZEP and (c) PMMA resists (20 nm scale bar). Images (d) and (e) show smallest linewidths achieved in SML 50 and ZEP, respectively (100 nm scale bar)

Figure 2: 5nm thick chromium metal lift-off using SML 50 (a) and ZEP (b) (100 nm scale bar). Gratings etched into Si via ICP etch for 1 minute using SML 50 (c) and ZEP (d) resists (300 nm scale bar)

Figure 3: Etch rates of the SML 300 (dashed) and ZEP (solid) at time intervals of 1, 3, 5 and 7 minutes via ICP etch

Voltage (kV)	SML 50		SML 100		SML 300		Cold Development	
	D_1	γ	D_1	γ	D_1	γ	D_1	γ
10	63	9.2	72	7.0	102	10.4	280	7.7
15	84	9.0	108	9.0	143	9.8	369	9.2
20	103	9.0	129	10.4	194	8.2	397	11.3
25	111	8.8	156	8.9	218	7.0	563	14.8
50	398	8.6	378	6.7	480	7.9	-	-

Table 1

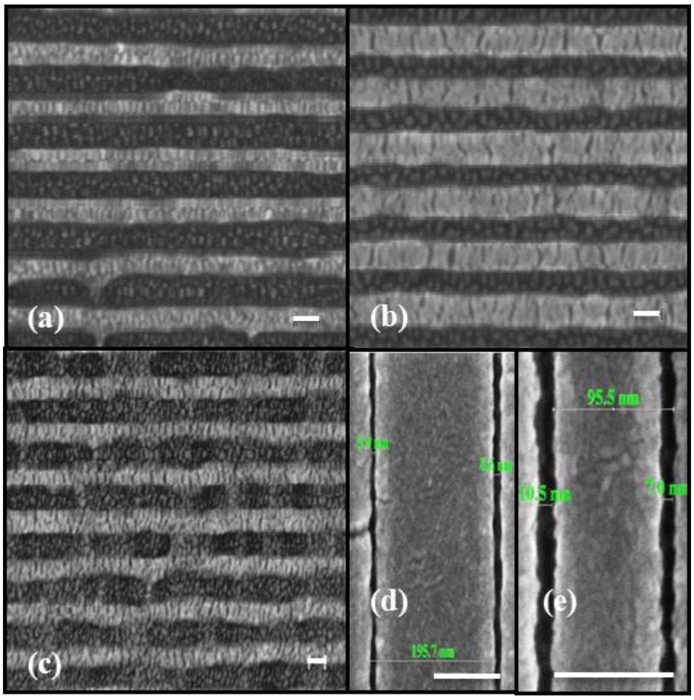

Figure 1

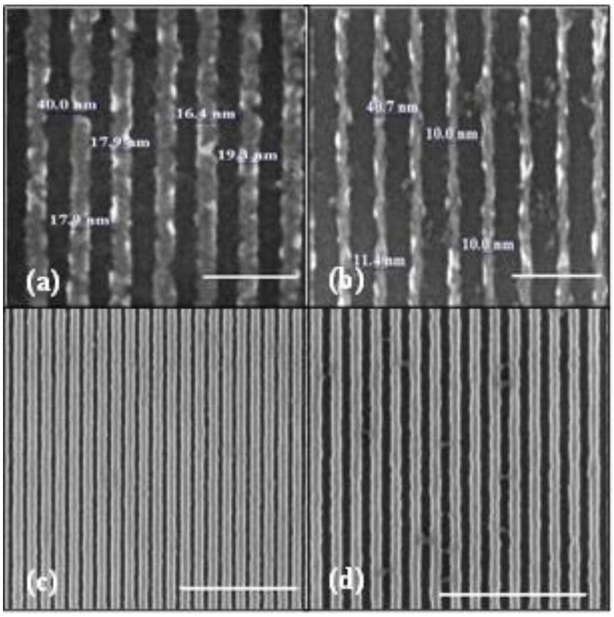

Figure 2

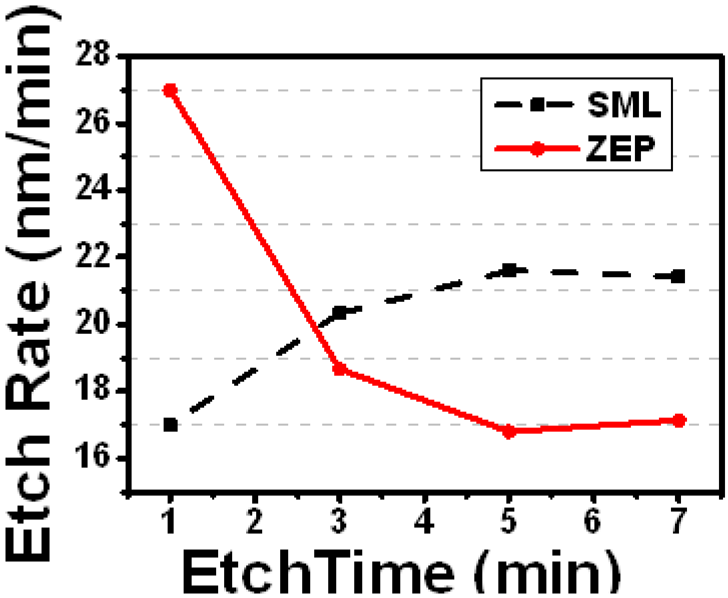

Figure 3

Graphical Abstract